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THE EFFECT OF MA/MAPE COMBINATION AS COUPLING AGENT IN FORMATION OF RICE HUSK AND RECYCLED HDPE-BASED COMPOSITES

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ABSTRACT

In this study, composites were made from source of recycled HDPE and rice husk as filler as well as addition of double coupling agent in order to improve mechanical properties of produced composites. The aim of this study is to know the effect of addition of double coupling agent of maleic anhydride (MA) and maleic anhydride polyethylene (MAPE) on quality of produced composites. In this research, the ratio of MA and MAPE that applied are 1:1; 1:2 and 2:1. The hot press method was used in order to form these composites. The composite formation process was perfomed at medium temperature of 170 ^{o}C for 30 minutes. After pressed manually and heated at these temperature later composite samples were cooled to room temperature naturally, and finally composites were tested to know its mechanical properties of tensile strength and bending strength as well as water absorption capacity. The results showed that the simultant addition of MA and MAPE as double coupling agent can improve the quality of the produced composites. The amount of MAPE that is added in MA coupling agent affected both the value of the tensile strength and bonding strength of the composites. The similar characterstics also occurred on property of water absorption on immersed composite. By addition of the MAPE and MA together then both coupling agents are increasing bonding adhesion between matrix and filler becomes stronger and tighter. The highest value of tensile strength of 5.75 MPa was obtained on the composite ratio of MA:MAPE= 1:2. While the highest value of bending strength of 4.1 MPa was also obtained on the composite with the same ratio. The highest water absorption of produced composites was found on composite by adding of ratio MA:MAPE=2:1 that is 9.4%.

Key words: rice husk, polyethylene, composite, MA and MAPE

Introduction

In this decade, the use of biomasssa-based materials as a reinforcing material (filler) in the composite manufacturing process has attracted many researchers to do so. Biomass material has many advantages such as low density, low cost, renewable and recyclable and biodegradability properties (Roger M. R, 2007). However, the main disadvantage of biomass materials in composites is the difficulty of achieving good dispersion during the mixing process, the composite susceptibility to moisture absorption, biomass material incompatibility between hydrophilic and hydrophobic polymers, resistance at low temperatures and inconsistencies in quality (Caulfield, D.F., et al ., 2005).

As fact the abundance of plastic waste in the environment, the manufacture of composites by using matrix of recycled plastic in addition to delivering innovative products to substitute the more expensive wood can also reduce the environmental load due to the plastic waste. The incorporation of biomass-based filler into recycled polyethylene as matrix would produce the composite with less and weak mechanical properties (Farid M., 2011). This is because the interface bonding that occurs as a result of the incorporation of biomass with hydrophilic property and polyethylene matrix with hydrophobic property is not perfect and also has low compatibility. To improve the compatibility of the two phases in the composite, it can be done by modification of the surface of the biomass either physical or chemical way. Chemical modification is often carried out to optimize the fiber interface. By introducing chemical modifications, an activated hydroxyl group or a new hydroxyl group is introduced that can effectively interact with the matrix. Chemical modification of the natural biomass that aims to improve the adhesion to the polymer matrix has been investigated by several researchers such as by (Bledzkia K. et al 1998, Pickering K.L. 2003, Qiu M., et al 2005, Shu M. and Li S. 2006, and John Z.L., et al 2005).

In order to increase the affinity and adhesion between rice husk and thermoplastic matrix, the coupling agent is added as part of the chemical modification. Coupling agent can be used as a material modification to improve adhesion of the interface with the matrix to improve the spread of the particles and a decrease in the water absorption properties of the resulting composites (Kamal, B.A, et al., 2008). The addition of coupling agent would improve the physical and mechanical properties of the composites. To enhance bonding interaction between matrix with an organic filler, some previous researchers have used various types of the coupling agents such as (Bledzkia K. et al 1998, Fatanah U. 2011, Nurhajati D.W. and Indrajati I.N. 2011, Farid M. 2012a) using maleic anhydride as a coupling agent, (Pickering K.L. 2003, Qiu M. et al. 2005, and Shu M. and Li S. 2006) added isocyanate coupling agent while (Sameni, J.K. et al. 2004, John Z. L. et al 2005, Prachayawarakorn J. et al. 2008, Farid M. 2012b) using maleic anhydride based polymers such as maleic anhydride polyethylene (MAPE) and maleic anhydride polypropylene (MAPP) in their research.

Some literatures state that the use of organic coupling agent types maleid anhydride (MA) or maleic anhydride with polyethylene plastic types (MAPE) are more suitable because they can increase the bond between the effective phase between a polar rice husk with a nonpolar polyethylene. However, based on the study of literature there has not been done the composite formation by the addition of both MA and MAPE together as coupling agent, so in this research effort to form composites with the addition of these two coupling agent simultaneously was performed. The aim of study is to know the effect of addition of double coupling agent of maleic anhydride (MA) and maleic anhydride poly ethylene (MAPE) with certain ratio on quality of produced composites especially on mechanical propertie of bending and tensile strength and water absorption capacity.

Materials and Methods

Equipments and Materials

The equipmens that are used included stirred reactor consisting of a three-neck flask (Pyrex), motor with stirrer (Fisher Scientific, maximum speed of 250 rpm), oil bath (Corning), hot press (hand made, temperature range of 29-300 ^{o}C), crusher and 100-200 mesh size sieve (Macross Testing sieve), oven with temperature range 25-400 ^{o}C (Gallenkamp), digital scales, 0-1000 gram (METLER Toledo), thermometer (0-200 °C), temperature control (50-500 °C). The materials used in the study are: rice husk as filler, recycled polyethylene as a matrix, xylene 20 % as a plastic solvent, maleic anhydride (MA) with M=98.05 g/mol and polyethylene-graft-maleic anhydride (MAPE) with density 0.92 g/ml, 12 mesh and MW 15,000 as a coupling agent. Rice husk was obtained from field in surrounding of Aceh Besar District, the same type and color of recycled HDPE plastics was collected from recycled collection point in around of Banda Aceh City.

Formation of Composites

Preparation of Matrix and Filler

In order to eliminate the extractive substances contained inside the rice husk taken from the field then rice husk previously was soaked in hot water at a temperature of 100 °C for 2 hours. During soaking the rice husk was mixed properly at medium rotation. After soaking, the rice husk was dried up naturally. Later rice husk was grinded and sieved with size of 100-200 mesh and then dried again using the oven at temperature of 105 °C for 24 hours until it reaches the water content of 2% - 3%, (Harper and Charles A., 1999). After getting dried the rice husk was kept in a desiccator to prevent contact with the outside air and also to absorb the remaining water contained in rice husks before composites manufacturing process. All collected recycled HDPE was cut into a small size of 0.5 cm x 0.5 cm then washed with detergent to clean recycled HDPE from contaminants. After that, recycled HDPE was rinsed with water and dried in the sun and finally in oven at temperature of 105 °C for 24 hours, (Harper and Charles A., 1999).

Formation of Composites

Formation of composites was performed by hot press method by using a hand made hot press equipped with manual press. Initially, 40 grams of cleaned and dried recycled HDPE was put in the three-neck flask and added little by little with 200 ml of xylene as solvent to melt HDPE (Caulfield DF, et al, 2005). Furthermore, the bath was turned on and the temperature was set around 145 ^{o}C. After the matrik getting melting well, then 60 grams of sieved and dried rice husk was added inside the flask and stirred rigorously until both materials mixed homogeneously for about 20 minutes. Inside the flask combination of MA and MAPE were also added as as much as 2, 3, 4 and 6 % by weight. The rasio of added MA/MAPE was varied with ratio of 1:1; 1:2 and 2:1. Later, homogeneous mixture was removed from the flask and allowed to cool to room temperature until all solvent was evaporated (usually take place for 1-2 days). Further compression process was carried out by using a hot press at a temperature of 170 °C for 30 min (Farid M. 2013). Composites then was cooled naturally and finally was tested.

Testing and Analysis

Tensile strength was tested in accordance with ASTM 638-99 Type I and bending strength was measured by using a Universal Testing Machine Electronic System Type: SC-2DE Japan in Laboratory of Research Center, Faculty of Mathematics and Natural Sciences University of North Sumatra, Medan. Water absorption test was performed in Laboratory of Technology Process, Chemical Engineering Depatment Faculty of Engineering Syiah Kuala University, Darussalam – Banda Aceh as procedure written in SNI 03-2105-1996.

Results and Discussion

Mechanical Properties of Composites

Maleic anhydride (MA) is as a bridge to combine cellulose and polyethylene with the presence of a free radical initiator. MA that is unsaturated vinyl compounds have chemical properties that is the special bond with the carboxyl clusters in it and this bond play role in the addition reaction. Besides, other literature by Sameni, J.K. et al., 2004 also confirmed that polyethylene-graft-maleic anhydride (MAPE) is an effective and suitable coupling agent to produce composites based on a matrix of HDPE polymer. MAPE has been used as a coupling agent to improve the adhesion bonding between ligno-cellulosic fiber derived from biomass-based filler and plastics based matrix.

To understand the effect of MA and MAPE combination on properties of produced composites, two kinds of mechanical properties (bending strength and tensile strength) were tested and analyzed on all prepared samples. Theoritically, mechanical properties of composites are associated with ability of composite to resist external forces that acting on the composite. The results of bending strength and tensile strength value from this study were later compared to the standard of SNI 03-2105-1996. According to SNI 03-2105-1996, the bending strength and the tensile strength of minimum standards that allowed is 9.81 MPa and 0.15 MPa, respectively.

Figure 1 shows results of bending strength for all composites at different ratio of MA/MAPE with matrix of recycled HDPE and filler of rice husk.

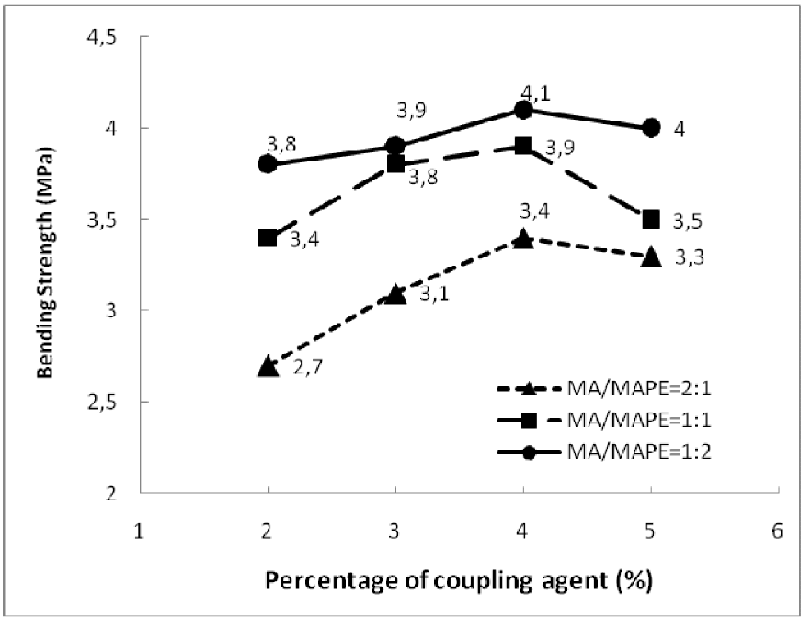

Figure 1. The effect of percentage of coupling agent (CA) and different ratio of MA/MAPE toward bending strength value on prepared composites

Figure 1 shows that the higher of bending strength value for recycled HDPE-based composites was obtained on composites with ratio of MA/MAPE coupling agent equal to 1:2. The second higher of bending strength value was on composites with ratio of MA/MAPE coupling agent equal to 1:1. And the lower one was on composites with ratio of MA/MAPE coupling agent equal to 2:1. Figure 1 also shows that the optimum of bending strength value for those composites was obtained at addition of 4 wt% of mixed coupling agent (MA and MAPE). Figure 1 indicated that the increasing of percentage of coupling agent would also increased the value of the bending strength where the maximum value of 4.1 MPa was obtained at addition of 4% wt MA and MAPE.

The presence of both MA and MAPE content in the mixture resulted in increasing of adhesion properties between rice husk with HDPE due to the esterification process between the anhydride groups of MA and MAPE with the hydroxyl group of rice husk. However by increasing the percentage of coupling agent until 6% wt will not increase the value of the bending strength. Kamal et al., 2008 also found that the addition of coupling agent increase bending strength and composites stiffness significantly. Bending strength value in composite with MAPE coupling agent increased if compared with composites without using MAPE (Farid M. 2012b). This is because the addition of MAPE has improved compatibility between filler and HDPE which in this case also reduces the absorption of water and increase the stability and mechanical properties of composites. From the results above, it was found that bending strength of composites by using recycled HDPE does not meet yet the standard of SNI 03-2105-1996.

Figure 2 shows results of tensile strength for all composites at different ratio of MA/MAPE and percentage of coupling agent with matrix of recycled HDPE and filler of rice husk.

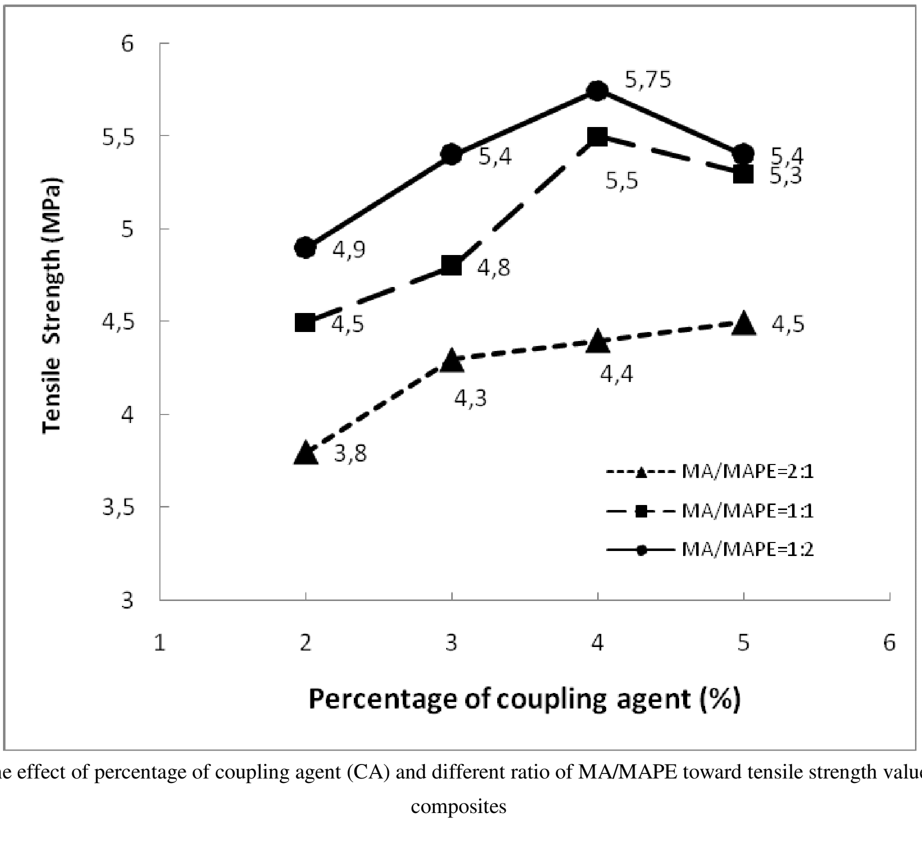

Figure 2. The effect of percentage of coupling agent (CA) and different ratio of MA/MAPE toward tensile strength value on prepared composites

From the above figure it is known that tensile strength value increased with increasing percentage of couling agent at any ratio of MA/MAPE. The higher tensile strength value was obtained at composites prepared with addition of MA/MAPE ratio of 1:2 following with addition of MA/MAPE ratio of 1:1 and addition of MA/MAPE ratio of 2:1, respectively. It was observed from Figure 2 that the optimum of tensile strength value for all prepared composites was found at addition of 4 wt% of mixed coupling agent (MA and MAPE). The highest tensile strength value of those composites with recycled HDPE matrix at addition of 4 wt% of coupling agent was 5.75 MPa. On the other hand the lowest tensile strength value of those composites was 3.8 MPa at addition of 2 wt% of mixed coupling agent (MA and MAPE). Kamal et al., 2008 found that an increase of tensile strength due to the formation of ester bonds between carbonyl groups of the anhydride of coupling agent and the hydroxyl groups of the filler. However, the amount of coupling agent had a significant effect on tensile strength value, which means that the addition of coupling agent increases the tensile strength value due to an increase of adhesion bonding between the matrix and the filler.

As in our above result after addition 6 wt% of mixed coupling agent the tensile strength value became decreasing, and Prachayawarakorn et al., 2008 also found a decline in tensile strength value after addition of excess coupling agent caused low blending component interface interaction, which would lead to the outbreak of the mechanical structure of the mixed interface. Another result by Keener TJ, et al., 2004 mentioned that the value of the tensile strength of the composite decreases with increasing content of coupling agent added. This is because the higher the amount of coupling agent in the composite, the bond that has been formed with strong between matrix and fillers will weaken again due to shortage formed composite adhesive number (matrix) is needed or the clotting process in the composite. This in turn makes the bond interface becomes weak and consequently will reduce the value of the tensile strength and modulus values are also broken. Nevertheless both bending strengh and tensile strength some values slightly deviate can occur because of incomplete mixing between the filler and matrix to form air bubbles in the composite more or insufficient pressure exerted during the compression process heat is accompanied by pressing especially in the manufacturing process we use manually pressing process. From the above results, it is known that tensile strength value of composite meets the standards according to SNI 03-2105-1996.

To know the nature of resistance to water absorption in all prepared composites when it was immersed in water then we also did testing of water absorption in which all of result test were shown in Figure 3.

Composite board is a substance that has the hygroscopis properties so that it is able to absorb moisture from the surrounding environment to achieve equilibrium and likewise when composite board was immersed in water it would expand. Water absorption capacity was determined based on the weight of the specimens after being immersed for a day in accordance with the method requirement in SNI 03-2105-1996. The results showed that the water absorption capacity on average range from 5% - 9.4%, which these results indicated that the water absorption capacity in all prepared composite board met SNI 03-2105-1996. Figure 3 also showed that the prepared composite with the addition of a more dominant MA than MAPE gives the water absorption is much higher compared with addition of a more MAPE coupling agent than MA.

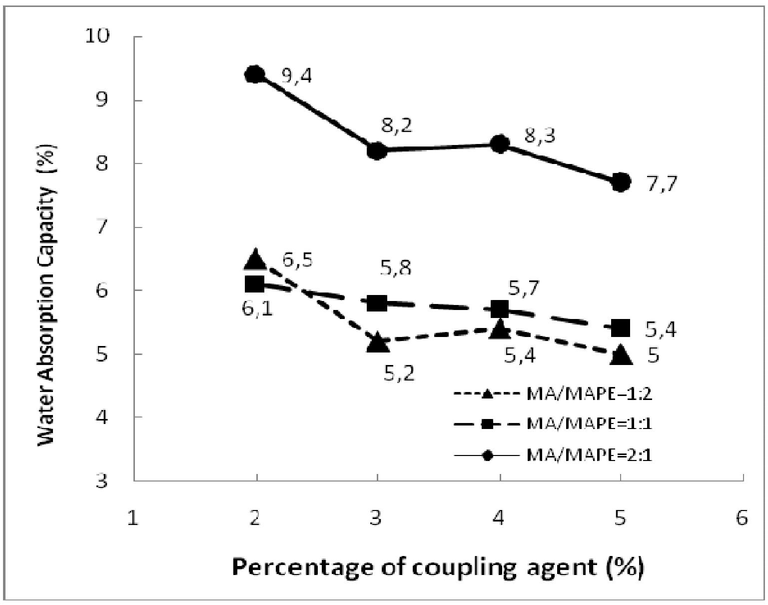

Figure 3. The relationship between percentage of coupling agent (CA) and different ratio of MA/MAPE toward water absorption capacity (%) on prepared composites

The effect of Coupling Agent

The literature states that the coupling agent is a substance that is used to modify the surface of the filler so that the bonding between the filler and the matrix can occur properly (Choi, et al, 2006). And for a typed coupling agent of maleid anhydride (MA) and polyethylene-graft-maleic anhydride (MAPE) were found that both couling agents have also been widely used to improve the adhesion bond between ligno-cellulosic fiber that comes from biomass-based filler and plastics-based matrix (Sameni, et al, 2004). So on the basis of the literature review in this study, the use of MA and MAPE has been conducted to improve the mechanical properties of the composite. Results of studies using both coupling agent showed that the use of each MA and MAPE generally produced a better composite properties namely the mechanical properties. For example in Farid M, 2012b the maximum value for the tensile strength of rice husk-based composites by the addition of maleid anhydride was 3.92 MPa while the composites that were made without the addition of maleid anhydride was only equal to 3.24 MPa. From the comparison of these results it can be concluded that the composites that uses a coupling agent has greater tensile strength value compared with those not using a coupling agent.

With regard to the results of current research, as can be seen in Figures 1 and 2, it indicated that the percentage of coupling agent that was added during preparation of composites affected significantly the value of mechanical propertiesnya as had already discussed above. Meanwhile for the influence of the added coupling agent ratio (MA/MAPE) can also be seen all all figures. Both Figure 1 and Figure 2 showed clearly that the addition of higher MAPE coupling agent than MA couling agent (ratio MA/MAPE = 2: 1) provided an understanding to us that formed composites resulted in higher of tensile and bending strength values, yet to determine the cause of a this happening needs further research and analysis of data regarding to functional group, morphology or thermal testing to address this issue in more detail.

Conclusions

The optimum of tensile and bending strength value for those composites was obtained at addition of 4 wt% of mixed coupling agent (MA and MAPE) and the highest of tensile and bending strength value for recycled HDPE-based composites was obtained on composites with ratio of MA/MAPE coupling agent equal to 1:2. The highest bending and tensile strength value of those composites with recycled HDPE matrix at addition of 4 wt% of coupling agent was 5.75 MPa and 4.1 MPa, respectively. Tensile strength values of composites met the minimum standards of SNI 03-2105-1996 but the bending strength values did not met. The presence of coupling agent content in composites resulted in increased adhesion properties between rice husk and HDPE thereby increasing the mechanical physical properties of composites. The water absorption capacity of all prepared composite was on average range of 5% - 9.4% and these values meet SNI 03-2105-1996.

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